The present invention is directed to a method for recovering a precious metal from a precious metal-containing material using a leaching agent and one or more oxidants. The leaching agent is preferably thiosulfate and the oxidants one or more of chloride (ClO₂⁻), chlorate (ClO₃⁻), bromate (BrO₃⁻), iodate (IO₃⁻), ferric oxide (Fe₂O₃), chromate (CrO₄²⁻) and manganese dioxide (MnO₂). The invention is particularly suitable for in situ mining or leaching of precious metal deposits.
Fig. 1

Barren Lixiviant

Introduce Lixiviant into Injection Wells

Pregnant Leach Solution

Collect Pregnant Leach Solution from Collection Wells

Collected Pregnant Leach Solution

Precious Metal Recovery

Precious Metal

Barren Solution

Add Fresh Leaching Agent and Oxidant

Fig. 3
Two ports (with caps to provide sealing) for the introduction of feed, taking samples, and inserting the electrodes (pH, ORP, and DO).

Sealed Shaft connected to a mixer.

N2 port for the purging of the gas space.

Body and flanges are made of Lexan. The lid is made of PVC.

Dip Tube for N2 purging of the Slurry.

3/4" pipe for valve connection for drain.

Fig. 4
Figure 5: Effect of chlorate on gold extraction vs. time for the FNR ore in ammonium thiosulfate solution.
Figure 6: Effect of chlorate on thiosulfate concentration vs. time for the FNR ore in ammonium thiosulfate solution.
Figure 7: Effect of chlorate on gold extraction vs. time for the CO ore in ammonium thiosulfate solution.
Figure 8: Effect of chlorate on thiosulfate concentration vs. time for the CO ore in ammonium thiosulfate solution.
Figure 9: Effect of chlorate on gold extraction vs. time for the CO ore in calcium thiosulfate solution.
Figure 10: Effect of chlorate on thiosulfate concentration vs. time for the CO ore in calcium thiosulfate solution.
Figure 11: Effect of chlorate on gold extraction vs. time for the NCO ore in ammonium thiosulfate solution.
Figure 12: Effect of chlorate on thiosulfate concentration vs. time for the NCO ore in ammonium thiosulfate solution.
Figure 13: Effect of manganese dioxide on gold extraction vs. time for the FNR ore in ammonium thiosulfate solution.
Figure 14: Effect of manganese dioxide on thiosulfate concentration vs. time for the FNR ore in ammonium thiosulfate solution.
ANOXIC LEACHING OF PRECIOUS METALS WITH THIOSULFATE AND PRECIOUS METAL OXIDANTS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] Cross reference is made to U.S. patent application Ser. No. 09/852,609, filed May 11, 2001, entitled “METHOD FOR THIOSULFATE LEACHING OF PRECIOUS METAL-CONTAINING MATERIALS” to Ji et al., which contains related subject matter and is incorporated herein by this reference.

FIELD OF THE INVENTION

[0002] The present application is related generally to leaching and specifically to leaching of precious metals.

BACKGROUND OF THE INVENTION

[0003] As unmined precious metal-containing materials continue to drop in grade worldwide, mining companies are facing increasing challenges with developing low cost mining techniques capable of mining such materials at a profit. As used herein, “precious metals” refers to the transition elements gold, silver, the platinum group metals, and combinations thereof. In situ or solution mining techniques have been explored as a methodology for recovering precious metals from underground precious metal-bearing deposits inexpensively.

[0004] In solution mining, a first series of injection wells are used to introduce a leaching solution or lixiviant into the deposit at spaced apart locations and a second series of collection wells, positioned so as to be in fluid connection with one or more adjacent injection wells, are used to collect and withdraw a pregnant leach solution from the orebody. The pregnant leach solution is formed by the lixiviant percolating through the permeable ore body, such permeability being either from natural or induced porosity and oxidizing precious metal-containing minerals or elemental precious metal, so that the precious metal is solubilized by or dissolved into the lixiviant. The precious metal is recovered from the collected pregnant leach solution by conventional techniques. As will be appreciated, excavations can be used rather than or in addition to wells for introducing the lixiviant and collecting the pregnant leach solution.

[0005] A recurring problem in in situ leaching operations is the maintenance of oxidizing conditions as the lixiviant traverses the orebody. Typically, the oxidants in the lixiviant are consumed rapidly after the lixiviant contacts the orebody. This rapid consumption is due not only to the reaction of the oxidant(s) with numerous precious metal-barron minerals in the orebody but also with other components of the lixiviant itself. For example, leaching agent such as thiosulfate can be oxidized readily by oxidants, such as molecular oxygen. The failure to maintain oxidizing conditions throughout the orebody can lead to low leaching rates and precious metal recoveries.

[0006] Another recurring problem in in situ leaching operations is the potential contamination of water-containing aquifers by the lixiviant. This is potentially problematical for lixiviants that are highly toxic, such as cyanide.

SUMMARY OF THE INVENTION

[0007] These and other needs are addressed by the various embodiments and configurations of the present invention. The present invention is directed to oxidants, other than molecular oxygen, for use with various leaching agents for recovering precious metals.

[0008] In one embodiment, a method for recovering a precious metal from a precious metal-containing material is provided that includes the steps of:

[0009] (a) providing a lixiviant, the lixiviant including thiosulfate and an oxidant that is at least one of chlorite (ClO$_2^-$), chlorate (ClO$_3^-$), bromate (BrO$_3^-$), iodate (IO$_3^-$), manganese dioxide (MnO$_2$), ferric oxide (Fe$_2$O$_3$), and chromate (CrO$_4^{2-}$); and

[0010] (b) contacting the lixiviant with the precious metal-containing material to dissolve the precious metal and form a pregnant leach solution. The method is particularly useful for solution mining or in situ leaching of precious metal deposits which are performed under anoxic conditions. The oxidant is typically effective enough that molecular oxygen or other more aggressive oxidants are not required to effect precious metal dissolution in the lixiviant. The oxidants may be deliberately added or may already be present in the precious metal-bearing material and/or in the groundwater that comes into contact with the precious metal-bearing material.

[0011] In a preferred process configuration, the lixiviant is a thiosulfate salt. For example, the thiosulfate salt can be one or more of ammonium thiosulfate, sodium thiosulfate, potassium thiosulfate, and calcium thiosulfate. Non-ammonium thiosulfate salts are particularly attractive where potential ammonia/ammonium groundwater contamination is of concern. In addition to the oxidant, the thiosulfate lixiviant can include cupric ion, ammonium ion, ammonia, and/or sulfite ion.

[0012] For solution mining or in situ applications or applications in which an oxidant is in insoluble form, the lixiviant can include one or more of suspension agents, gelling agents, thickening agents, and surfactants.

[0013] The process can have a number of advantages, particularly when compared to existing precious metal solution mining or in situ leaching processes. For example, the oxidants can maintain oxidizing conditions as the lixiviant traverses the orebody and in the absence or virtual absence of (dissolved) molecular oxygen. The oxidants are relatively mild (due to kinetic and/or thermodynamic factors) and are generally not consumed rapidly after the lixiviant contacts the orebody. The oxidant is highly reactive with either the numerous precious metal-barron minerals in the orebody or other components of the lixiviant itself. For example, leaching agents such as thiosulfate and iodide are typically not oxidized readily by the above oxidants as in the case of dissolved molecular oxygen or cupric tetraammine. The maintenance of oxidizing conditions throughout the orebody can lead to high leaching rates and precious metal recoveries. The leaching agents and oxidants are generally not highly toxic and are environmentally acceptable. Accordingly, the danger of harmful contamination of water-containing aquifers by the lixiviant are reduced relative to many other leaching agents/oxidants.

[0014] These and other advantages will be apparent from the disclosure of the invention(s) contained herein.
The above-described embodiments and configurations are neither complete nor exhaustive. As will be appreciated, other embodiments of the invention are possible utilizing, alone or in combination, one or more of the features set forth above or described in detail below.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a plan view, according to a first embodiment of the present invention, of a solution mining system being used to recover a precious metal from a placer deposit;

FIG. 2 is a cross-sectional view along line 2-2 of FIG. 1;

FIG. 3 is a flowchart of the solution mining leaching process of the first embodiment of the present invention;

FIG. 4 depicts the experimental apparatus used in the experimental work discussed below;

FIG. 5 is a plot of gold leached (vertical axis) against time (horizontal axis) for an ammonium thiosulfate/chlorate leaching system;

FIG. 6 is a plot of thiosulfate concentration (vertical axis) against time (horizontal axis) for the leaching system of FIG. 5;

FIG. 7 is a plot of gold leached (vertical axis) against time (horizontal axis) for an ammonium thiosulfate/chlorate leaching system;

FIG. 8 is a plot of thiosulfate concentration (vertical axis) against time (horizontal axis) for the leaching system of FIG. 7;

FIG. 9 is a plot of gold leached (vertical axis) against time (horizontal axis) for an ammonium thiosulfate/chlorate leaching system;

FIG. 10 is a plot of thiosulfate concentration (vertical axis) against time (horizontal axis) for the leaching system of FIG. 9;

FIG. 11 is a plot of gold leached (vertical axis) against time (horizontal axis) for an ammonium thiosulfate/chlorate leaching system;

FIG. 12 is a plot of thiosulfate concentration (vertical axis) against time (horizontal axis) for the leaching system of FIG. 11;

FIG. 13 is a plot of gold leached (vertical axis) against time (horizontal axis) for an ammonium thiosulfate/manganese dioxide leaching system; and

FIG. 14 is a plot of thiosulfate concentration (vertical axis) against time (horizontal axis) for the leaching system of FIG. 13.

DETAILED DESCRIPTION

The present invention can be used to extract precious metals from precious metal-containing materials. The present invention is particularly advantageous in recovering precious metals from sulfide and/or oxide ores, whether or not the ores contain carbon or are igneous, metamorphic, or sedimentary in origin.

FIGS. 1 and 2 show a solution mining system 100 according to a first embodiment of the present invention. A plurality of injection wells 104a-n for introducing a lixiviant into the deposit 108 at one or more locations along the length of the well, and a plurality of collection (or production) wells 112a-s for collecting pregnant leach solution, formed by percolation of the lixiviant through the orebody 108, at one or more locations along the length of the well. As will be appreciated, the wells may include screens to prevent clogging of the well by debris loosened by the lixiviant/pregnant leach solution, and the formation adjacent to the well may be (hydro)fractured and propped open by suitable techniques to increase the rate of travel of the lixiviant/pregnant leach solution through the orebody. Although not shown, measures such as forming and using vertical boundary walls such as disclosed by U.S. Pat. No. 4,311,340, injecting water into guard wells, forming and filling void areas with a plugging material such as disclosed by U.S. Pat. No. 4,289,354, or utilizing some other type of impermeable barrier such as disclosed by U.S. Pat. No. 4,634,187 may be employed to confine the lixiviant/pregnant leach solution to a defined part of the orebody.

Although a “line drive” pattern is shown in FIG. 1 in which the injection wells are arranged in a line so that the injected lixiviant advances through the deposit toward one or more spaced production wells that may also be arranged in a line substantially parallel to the line of the injection wells, any pattern may be employed depending on the application. For example, the pattern can be a “five spot” pattern in which a central production well is surrounded by four somewhat symmetrically located injection wells. Examples of other suitable patterns include staggered line drive, four spot, seven spot, circular flood patterns.

To drive the lixiviant towards production wells, a suitable pressure differential may be established between the two types of wells. Typically, the production wells will have a greater draw pressure than the injection pressure of the adjacent injection well(s). As will be appreciated, the draw and collection pressures may also be substantially equivalent, or the draw pressure may exceed the collection pressure, depending on the application.

The system 100 further includes a pregnant leach solution holding tank 116, a precious metal recovery facility 120, and a lixiviant preparation vessel 124. The holding tank 116, which can be in the form of a holding pond, receives and holds collected pregnant leach solution until the recovery facility 120 is able to treat the pregnant leach solution. The recovery facility 120 recovers the precious metal from the pregnant leach solution and forms a precious metal product and a barren solution that is reintroduced into the formation. The facility 120 can effect precious metal recovery by any suitable technique, such as cementation, sulfide precipitation, carbon adsorption/elution, resin adsorption/elution, and electrowinning. The pregnant solution flows through the facility 120 as shown by arrows 128, 132, and 136. Vessel 124 is typically a stirred tank and combines the various constituents of the lixiviant for addition to and replenishment of the barren solution.

The lixiviant 300 (FIG. 3) preferably includes a leaching agent and one or more oxidants other than or in addition to molecular oxygen. To avoid contamination of ground water and consequent environmental damage, the
lixiviant preferably does not include a highly toxic constituent. To avoid dissolution of unwanted minerals and excessive use of buffering solutions, it is preferred to select the lixiviant constituents to provide a pH of the lixiviant that is close to neutral pH. The pH of the lixiviant is more preferably at least about pH 6 and even more preferably from about pH 6.5 to about pH 12. To avoid thermal incompatibility of the lixiviant with the deposit, the lixiviant constituents are selected so as to be effective in dissolving precious metals at or near the ambient rock temperature, which, of course, depends on the depth of the deposit. Typically, the operating range of the lixiviant will range from about 0°C to about 75°C.

[0036] To provide these properties, the leaching agent is preferably one or more of thiosulfate (S₂O₃²⁻), a halogen such as chloride (Cl⁻), iodide (I⁻) and bromide (Br⁻), and malononitrile (HC₂N(CN)₂). The thiosulfate or iodide anion is preferably in the form of a salt, typically compounded with one or more of ammonium cation or an alkali or alkaline earth metal cation, such as potassium, sodium, and calcium. Alternatively, the halogen can be present in elemental form which will be reduced to an anion by a halogen reducing species present in the precious metal-containing material or orebody 108, such as base metal sulfides. Iodine and bromine are typically introduced in the lixiviant in the form of an anion and as an element (iodide or bromide). Malononitrile, halogens, and thiosulfate are particularly preferred, with thiosulfate being even more preferred, due to its effectiveness at pH 7 and higher, which is the natural pH range for most precious metal-containing deposits. The preferred concentration of the leaching agent in the lixiviant is preferably at least about 0.01 M and more preferably ranges from about 0.1 to about 0.5 M.

[0037] While not wishing to be bound by any theory, the chemical equations governing the reactions of the various leaching agents with precious metals are set forth below for gold as the precious metal.

[0038] For thiosulfate:

\[ \text{Au} + 2 \text{S}_2\text{O}_3^{2-} + \text{I}_2 + \text{H}_2\text{O} \rightarrow \text{Au(S}_2\text{O}_3)_2^{2-} + \text{OH}^- + \text{I}^- \]  (1)

[0039] For halogens (with iodine as an example):

\[ 2\text{Au} + \text{I}_2 \rightarrow 2\text{AuI} \]  (2)

[0040] For malononitrile:

\[ \text{CH}_2\text{(CN)}_2 + \text{OH}^- \rightarrow \text{CH}_2\text{(CN)}_2^- + \text{H}_2\text{O} \]  (3)

\[ \text{Au} + 2\text{CH}_2\text{(CN)}_2^- \rightarrow \text{Au(CH}_2\text{(CN)}_2)_2^- + \text{e}^- \]  (4)

\[ \text{Au} + \text{CH}_2\text{(CN)}_2^- + \text{H}_2\text{O} \rightarrow \text{Au(CH}_2\text{(CN)}_2)_2^- + \text{e}^- \]  (5)

[0041] The oxidant(s) in the lixiviant preferably do not react rapidly with the deposit or orebody 108 after contact with the deposit. Certain oxidants, such as dissolved molecular oxygen, are consumed too rapidly by reaction with the various minerals in the deposit and are therefore unable to dissolve precious metals located at some distance from the injection well. However, other oxidants have been found to have greater longevity after introduction into the deposit and more selectivity in reacting with precious metal-containing minerals as opposed to gangue minerals. These oxidants are also less reactive with the leaching agent, particularly thiosulfate, which not only substantially minimizes thiosulfate loss and formation of deleterious compounds, such as tetrathionates and other polythionates, but also avoids unnecessary oxidant consumption. Preferred oxidants include the anions, chlorite (ClO₃⁻), chlorate (ClO₄⁻), bromate (BrO₅⁻), iodate (IO₅⁻), an oxide of an element of Group VII B of the Periodic Table of the Elements such as chromate (CrO₄²⁻), an oxide of an element of Group VII B of the Periodic Table of the Elements, such as the compound manganese dioxide (MnO₂), an oxide of an element of Group VIII of the Periodic Table of the Elements such as ferric oxide (Fe₂O₃) and precursors thereof, with the anions chlorite (ClO₃⁻), chlorate (ClO₄⁻), bromate (BrO₅⁻), iodate (IO₅⁻), and iodine (I₂), and the compound manganese dioxide (MnO₂) and precursors thereof being particularly preferred, and with the anions chlorate, bromate, iodate and manganese dioxide being particularly preferred for reasons of high effectiveness, low cost, and/or low toxicity. The above anions are typically in the form of a salt and more typically are compounded with one or more of ammonium cation or an alkali or alkaline earth metal cation, such as potassium, sodium, and calcium.

[0042] While not wishing to be bound by any theory, it is believed that the various oxidants facilitate gold dissolution being reduced according to the following half-cell reactions:

\[ \text{ClO}_3^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{ClO}_2^- + 2\text{OH}^- \]  (6)

\[ \text{ClO}_4^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{ClO}_3^- + 2\text{OH}^- \]  (7)

\[ \text{ClO}^- + \text{H}_2\text{O} + \text{e}^- \rightarrow \text{ClO}^- + 2\text{H}^- \]  (8)

\[ \text{MnO}_2 + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{OH}^- \]  (9)

\[ \text{CrO}_4^{2-} + 4\text{H}_2\text{O} + 3\text{e}^- \rightarrow \text{Cr(OH)}_3 + 5\text{OH}^- \]  (10)

\[ \text{Fe}_2\text{O}_3 + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{Fe(OH)}_2 + 2\text{OH}^- \]  (11)

[0044] It is surprising and unexpected that certain anions with high oxidation potentials, such as chlorate have been found to be less reactive with thiosulfate than related anions, such as chlorite and hypochlorite. While not wishing to be bound by any theory, it is believed that the reaction of chlorate with thiosulfate is more kinetically restricted as opposed to thermodynamically restricted when compared to the reactions of chlorite or hypochlorite with thiosulfate.

[0045] The preferred concentration of the oxidants depends, of course, on the solubility limits of the oxidants in the lixiviant. To provide a higher total (overall) concentration of oxidants in the lixiviant, a number of differing oxidants are typically included in the lixiviant. Preferably, the total concentration of dissolved oxidants (other than molecular oxygen) in the lixiviant are at least about 0.01 M and more preferably ranges from about 0.1 to about 0.5 M.

[0046] To increase the amount of oxidants in the lixiviant, the oxidants can also be added as finely ground sparingly soluble particles. To provide effective suspension of the oxidants in the lixiviant, the P₉₀ size of the particles is preferably no more than about 200 µm and more preferably is in the range of about 1 to about 100 µm. The concentration of the sparingly soluble particles in the lixiviant preferably is at least about 0.001 vol. % and even more preferably ranges from about 0.01 to about 1 vol. %.

[0047] Typically, though the lixiviant when introduced into the well may be saturated with molecular oxygen, the molecular oxygen is consumed rapidly after contact with the precious metal deposit to provide anoxic conditions. The molecular oxygen content of the lixiviant can fall rapidly to near zero. Typically, the lixiviant, when percolating or
traversing the deposit to a collection well will contain no more than about 5 ppm, even more typically no more than about 2.5 ppm molecular oxygen, and even more typically no more than about 1 ppm molecular oxygen.

[0048] To provide effective particle suspension, the lixiviant can include one or more suspension, gelling, or thickening agents known to those of skill in the art. As will be appreciated, “suspension agents” refer to materials that assist in suspending solid material in a liquid, liquid mixture, or solution; “gelling agents” refer to materials that interact, either physically (thickening) or chemically (polymerization), with a liquid, liquid mixture, or solution, and “thickening agents” refer to any of a variety of hydrophilic substances used to increase the viscosity of a liquid, liquid mixture, or solution and to aid in maintaining stability by their emulsifying properties. Thickening agents are generally in four classes, namely (i) starches, gums, casein, gelatin, and phyocolloids; (ii) semi-synthetic cellulose derivatives (such as carboxymethyl-cellulose, etc.); (iii) polyvinyl alcohol and carboxy-vinylates; and (iv) bentonite, silicates, and colloidal silica. Examples of suitable suspension, gelling or thickening agents include such natural materials as guar gum, xanthan gum, or karaya gum of such synthetic products as the ionic polysaccharide B-1450 produced by fermentation of glucose with the bacterium *xanthisomnas campestris* NNRRL B-1459, USDA, and poly(glucoxyglucan) such as disclosed in U.S. Pat. No. 3,372,749, carboxymethyl cellulose, polyethyleneoxide, polyelectrolays, polycrylamide, butylsucrose copolymers, polycrylonitrile, hydroxyethyl cellulose, partially hydrolyzed polyacrylamides, starch suspensions, heavy metal phosphates, sodium borate, polyvinyl alcohols, and mixtures thereof. While the above are specific examples, it is understood that any suspension, gelling or thickening agent compatible with the formation involved and the lixiviant constituents may be employed in the present invention. When such an agent is employed, the viscosity of the aqueous lixiviant is preferably in the range of at least about 2 Cps. The desired viscosity is typically achieved using from about 0.5 to about 5 weight percent of such agents.

[0049] The lixiviant can also include one or more surface-active agents or surfactants. As will be appreciated, surfactants reduce surface tension when dissolved in water or water solutions (such as between the water constituent of the lixiviant and other lixiviant constituents) or reduce interfacial tension between two liquids (such as between liquid-phase lixiviant constituents) or between a liquid (such as the lixiviant) and a solid (such as the insoluble oxidant particles). Surfactants are generally in three categories, namely detergents, wetting agents, and emulsifiers. When a surfactant is employed, the surfactant concentration typically ranges from about 0.01 to about 1 wt. % of the lixiviant.

[0050] The lixiviant can include other components depending on the application. For example, when thiosulfate is the leaching agent the lixiviant can include one or more of cupric cation, free ammonia, ammonium cation, cupric ammine cation, and sulfite anion. The positive effects of these cations and anions in thiosulfate leaching are well known to one of ordinary skill in the art. The cupric ion in particular has been found to catalyze and increase the rate of the oxidation reaction between the oxidant and the precious metal. Preferably, the total cupric ion concentration is at least about 1 ppm and more preferably ranges from about 5 to about 100 ppm. Ammonia has been found not only to catalyze the leaching reaction between the lixiviant and the precious metal but also to stabilize the thiosulfate anion. Preferably, the free ammonia concentration is at least about 100 ppm and more preferably ranges from about 100 to about 1000 ppm. It is believed that the reducing agent sulfite may cause rapid consumption of the oxidant. Accordingly, it is preferable that the lixiviant be at least substantially free of sulfite and more preferably contain no more than about 1.0 ppm sulfite. A more detailed discussion of these cations and anions is in U.S. patent application Ser. No. 09/852,699 filed May 11, 2001, to Ji, et al., and entitled “METHOD FOR THIOSULFATE LEACHING OF PRECIOUS METAL-CONTAINING MATERIALS”, which is incorporated herein by this reference.

[0051] The operation of an embodiment of the present invention will now be discussed with reference to FIGS. 1-3.

[0052] In step 304, the lixiviant is introduced into the injection wells 104a-n. As shown in FIG. 2, the lixiviant is introduced into the orebody 108 around the periphery of the well and at various points of contact between the well and the orebody 108. The lixiviant moves radially outwardly from the well 104 through the orebody 108. The lixiviant is drawn through the orebody 108 towards an adjacent collection well 112 by a pressure differential between the injection well and the collection well. As the lixiviant traverses the orebody towards the collection well, the lixiviant dissolves precious metal(s) forming a pregnant leach solution 308. The time typically required for the lixiviant/pregnant leach solution to travel from an injection well to an adjacent collection well is about 1 hour to about 60 days, depending on the porosity and permeability of the orebody and the distance between the wells.

[0053] In step 312, the pregnant leach solution 308 is collected from various collection wells to form a collected pregnant leach solution 316. The collected pregnant leach solution 316 is transported by means of conduits 140 to the holding tank 116. As needed, the collected pregnant leach solution 316 is drawn from the holding tank and fed to the precious metal recovery facility 120.

[0054] In step 320, the pregnant leach solution 316 is subjected to precious metal recovery process(es) in the facility 120 producing a precious metal product 324 and a barren solution 328. The concentration of precious metal in the barren solution 328 is of course less than the precious metal concentration in the pregnant leach solution 316. Most (more than 50%) of the dissolved precious metal(s) in the collected pregnant leach solution is recovered as the precious metal product 324.

[0055] In step 332, the barren solution 328 is transported in the conduit 144 past the intersecting conduit 148 from the lixiviant preparation vessel 124. In the lixiviant preparation vessel, fresh lixiviant is prepared. In one embodiment, fresh aqueous thiosulfate is contacted under agitation with the other constituents for the lixiviant. For example, the thiosulfate is contacted with the oxidants, suspension agent, cupric ion, ammonium ion and ammonia. The fresh lixiviant is combined with the barren solution 328 in a ratio sufficient to replenish the consumed thiosulfate, oxidant(s), and other additives to form a barren lixiviant 300. The barren lixiviant 300 is introduced into the various injection wells as set above with reference to step 304.
Experimental

[0056] To conduct experiments for the testing of the thiosulfate/chlorate system under anoxic conditions, sealed stirred tank reactors under 1-10 psi inert gas (nitrogen) pressure were employed, as shown in FIG. 4. The body 400 of the tank was made from acrylic; the head 404 was made from PVC. A 1/15 hp overhead mixer (not shown) was used for agitation. In addition to the opening 408 for the mixer shaft 414, there were 5 other openings 412, 416, 420, 424, and 428 on the lid. One of the openings 412 was used for pH, ORP (oxidation/reduction potential), and DO (dissolved oxygen) probes. Three of the other openings 416, 420, and 424 were used for nitrogen gas injection/exit. One last opening 428 was used for feed introduction and sampling. A nitrogen gas cylinder was connected to two of the input gas ports (one supplies nitrogen to the gas phase and the other to the liquid phase through a dip tube) on the lid to de-oxygenate the slurry to 1 ppm and to maintain a 2 psig pressure. To make sure that the pressure inside the tank did not exceed certain limits during over-night operation, a relief valve was connected to one of the nitrogen gas ports. The valve was set to open at around 10 psig. A drain 432 was included to drain the contents of the reactor. The mixer assembly included stationary baffles 436 surrounding an impeller 440.

[0057] Three different ore samples were tested as follows:

[0058] A fresh, non-refractory gold oxide ore with a P_{90}=200 \mu m (cone-crushed, wet-ground, and gravity gold removed).

[0059] A carbonaceous gold oxide ore. This ore was dry ground in a rod-mill for 30 minutes. No gravity gold or coarse fraction was separated. The P_{90} was 357 \mu m.

[0060] A non-carbonaceous gold oxide ore. This ore was dry ground in a rod-mill for around 120 minutes. No gravity gold or coarse fraction was separated. The P_{90} was 353 \mu m.

[0061] As mentioned above, the carbonaceous and non-carbonaceous gold oxide ores were dry ground. Through dry grinding, obtaining a constant and uniform slurry density was more manageable. To make sure that the ore samples were not overheated during dry-grinding, the grinding procedure was stopped every 15 minutes and the temperature was checked. The ore samples were found to be near the ambient temperature.

[0062] These ores were analyzed for gold, major elements, iron, carbon and sulfur. Tables 1, 2, and 3 respectively, present these results.

[0063] Due to the gold nugget effect in the fresh, non-refractory ore and to a lesser extent in the other two oxide ores, the head assay for any experiment was calculated. This was done based on the sum of the gold in the residue, the gold in the final solution, and the gold in the solution and solid samples that were removed during the test. The gold leaching calculations are, therefore, based on the calculated head assay.

### Table 1

<table>
<thead>
<tr>
<th>Ore</th>
<th>Average Au (g/t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh, Non-Refractory Ore</td>
<td>1.22</td>
</tr>
<tr>
<td>Carbonaceous Oxide Ore</td>
<td>8.42</td>
</tr>
<tr>
<td>Non-Carbonaceous Oxide Ore</td>
<td>10.42</td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>Ore</th>
<th>Al</th>
<th>Ca</th>
<th>K</th>
<th>Mg</th>
<th>Na</th>
<th>Si/O2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh, Non-Refractory Ore</td>
<td>5.77</td>
<td>4.41</td>
<td>1.34</td>
<td>4.25</td>
<td>0.65</td>
<td>54.40</td>
</tr>
<tr>
<td>Carbonaceous Oxide Ore</td>
<td>4.43</td>
<td>7.68</td>
<td>1.92</td>
<td>3.07</td>
<td>0.14</td>
<td>58.50</td>
</tr>
<tr>
<td>Non-Carbonaceous Oxide Ore</td>
<td>3.40</td>
<td>0.74</td>
<td>1.51</td>
<td>0.36</td>
<td>0.13</td>
<td>84.60</td>
</tr>
</tbody>
</table>

### Table 3

<table>
<thead>
<tr>
<th>Ore</th>
<th>Fe (Total)</th>
<th>Fe (Ferrous)</th>
<th>C (Total)</th>
<th>C (Organic)</th>
<th>S (Total)</th>
<th>S (Sulfide)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh, Non-Refractory Ore</td>
<td>4.91</td>
<td>4.43</td>
<td>3.14</td>
<td>0.29</td>
<td>0.52</td>
<td>0.52</td>
</tr>
<tr>
<td>Carbonaceous Oxide Ore</td>
<td>2.26</td>
<td>0.45</td>
<td>4.27</td>
<td>1.59</td>
<td>0.15</td>
<td>N/A</td>
</tr>
<tr>
<td>Non-Carbonaceous Oxide Ore</td>
<td>1.57</td>
<td>0.25</td>
<td>0.24</td>
<td>0.04</td>
<td>0.04</td>
<td>N/A</td>
</tr>
</tbody>
</table>

[0066] In the tests, the effect of the thiosulfate/chlorate lixiviant system on gold leaching from the three different ores was investigated. Furthermore, two tests with calcium
thiosulfate (instead of ammonium thiosulfate) were performed to investigate the role of the ammonium ion in this process. The experimental conditions for the various tests are reported in Table 5. These tests can be divided into the following four groups:

- Fresh, non-refractory ore (FNR)/ammonium thiosulfate
- Carbonaceous ore (CO)/ammonium thiosulfate
- Carbonaceous ore (CO)/calcium thiosulfate
- Non-Carbonaceous oxide ore (NCO)/ammonium thiosulfate

These four groups of tests are separately discussed below.

### Table 4

<table>
<thead>
<tr>
<th>Test Code</th>
<th>Ore type</th>
<th>Solid Pulp Density</th>
<th>Thiosulfate</th>
<th>Salt</th>
<th>Oxidant</th>
<th>Initial ClO₃⁻ Conc., g/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>LPSTR-1f</td>
<td>FNR</td>
<td>25</td>
<td>(NH₄)₂S₂O₃</td>
<td>NaClO₃</td>
<td>8.35</td>
<td></td>
</tr>
<tr>
<td>LPSTR-1f-R1</td>
<td>FNR</td>
<td>25</td>
<td>(NH₄)₂S₂O₃</td>
<td>NaClO₃</td>
<td>8.35</td>
<td></td>
</tr>
<tr>
<td>LPSTR-1f-S</td>
<td>FNR</td>
<td>25</td>
<td>(NH₄)₂S₂O₃</td>
<td>NaClO₃</td>
<td>8.35</td>
<td></td>
</tr>
<tr>
<td>LPSTR-1f-T</td>
<td>FNR</td>
<td>25</td>
<td>(NH₄)₂S₂O₃</td>
<td>NaClO₃</td>
<td>8.35</td>
<td></td>
</tr>
<tr>
<td>LPSTR-1f-1</td>
<td>CO</td>
<td>40</td>
<td>(NH₄)₂S₂O₃</td>
<td>NaClO₃</td>
<td>8.35</td>
<td></td>
</tr>
<tr>
<td>LPSTR-1f-2</td>
<td>CO</td>
<td>40</td>
<td>(NH₄)₂S₂O₃</td>
<td>NaClO₃</td>
<td>8.35</td>
<td></td>
</tr>
<tr>
<td>LPSTR-1f-3</td>
<td>CO</td>
<td>40</td>
<td>(NH₄)₂S₂O₃</td>
<td>NaClO₃</td>
<td>8.35</td>
<td></td>
</tr>
<tr>
<td>LPSTR-1f-4</td>
<td>CO</td>
<td>40</td>
<td>(NH₄)₂S₂O₃</td>
<td>NaClO₃</td>
<td>8.35</td>
<td></td>
</tr>
</tbody>
</table>

[0072] FIGS. 5-6 depicts graphically the results of tests on FNR ore (1f, 1f-R1, and 1f-S). Test 1f-R1 was a duplicate of test 1f. In these two tests, sodium chlorate was used as the oxidant. Test TS-b was similar to test 1f except that no chlorate was used. As shown in FIG. 5, negligible gold was dissolved in test TS-b where no chlorate was used. Furthermore, the reproducibility of the leaching data for test 1f is excellent. FIG. 6 shows that thiosulfate had not undergone any measurable degradation during the course of the test (44 days). About 0.3 g/L each of tetraionate and triionate were detected in the 1f-R1 solution after 20 days. However, the concentration of those species did not increase anymore afterward.

[0073] It can be concluded for the FNR ore that the thiosulfate/chlorate leaching system is a robust system that can leach gold with minimal thiosulfate degradation. Four tests were performed on CO ore using ammonium thiosulfate and calcium thiosulfate.

[0074] Test TS-c was performed with 8.35 g/L of ClO₃⁻ and 22.4 g/L S₂O₃²⁻. In test TS-d, the same conditions as TS-c were used except that no chlorate was added. For both of these tests the CO ore was wet ground and the coarse fraction (+65 mesh or +210 μm) was removed. The ore was then added to the reactor as a slurry. In comparing the gold extraction results from FIG. 7, the following conclusions can be made:

- Up to 68% of the gold can be extracted without any oxidant (test TS-d).

Adding chlorate to the thiosulfate solution increased the extraction by about 10% after 30 days (test TS-e compared to the test TS-d).

[0077] FIG. 8 shows that only about 1 g/L of thiosulfate was degraded under chlorate conditions after 30 days.

[0078] Two tests were performed on the CO ore using calcium thiosulfate (tests TS-c and TS-f). As shown in FIG. 9, test TS-c with chlorate yielded 11% higher gold extraction compared to test TS-f with no chlorate added. In FIG. 9, the gold extractions from the tests TS-c and TS-d (with ammonium thiosulfate) are also shown for comparison. In both cases, with and without chlorate, the gold extraction using ammonium thiosulfate was 12 to 15% higher, compared to the calcium thiosulfate tests. However, FIG. 10 shows that calcium thiosulfate was somewhat more stable than the ammonium thiosulfate/chlorate system (TS-e).

[0079] Two tests were performed on NCO ore using ammonium thiosulfate. In test TS-g, 8.35 g/L chlorate was used whereas no chlorate was used in test TS-h. As shown in FIG. 11, around 43% of the gold was extracted in 29 days using chlorate as the oxidant, and the gold extraction was still increasing. In the case of no chlorate, the gold extraction was only about 5% after 21 days. As shown in FIG. 12, the thiosulfate concentration was stable over time. The unexpected increase in the thiosulfate concentration at about 350 hrs (FIG. 12) may have been due to a technical problem experienced with the analytical equipment used for measuring thiosulfate.

In other experiments, the effectiveness of manganese dioxides, which is insoluble in thiosulfate, was investigated using FNR ore. In test TSMn-A, 3.8 wt. % of manganese dioxide was added to an aqueous ammonium thiosulfate solution free of cupric ions. In test TSMn-B, 3.8 wt. % of manganese dioxide was added to an aqueous thiosulfate solution containing 50 ppm cupric ion. In test TSMn-b, the aqueous ammonium thiosulfate solution was free of manganese dioxide and cupric ions. In each of the tests, the concentration of ammonium thiosulfate was about 22 g/L. The manganese dioxide was ground to a F₅₀ of less than 100 μm.

[0081] The results of the experiments are shown in FIGS. 13-14. Referring to FIG. 13, with tests TSMn-A and TSMn-B, the gold extraction was zero for the first four days and then rose to about 33.5% over the next thirty-one days. The gold extraction was greatest in test TSMn-B, in the presence of cupric ion. In test TSMn-b, less than 5% of the gold was dissolved in twenty-five days. FIG. 14 shows that the concentration of thiosulfate remained relatively stable throughout the tests, indicating that the manganese dioxide caused little degradation of the thiosulfate.

[0082] To summarize, these results demonstrate that chlorate and manganese dioxide function as gold oxidants in thiosulfate media under substantially oxygen-free conditions.

[0083] A number of variations and modifications of the invention can be used. It would be possible to provide for some features of the invention without providing others.

[0084] For example in one alternative embodiment, the oxidants are used with thiosulfate to recover precious metals from excavated materials. In this embodiment, the recovery
may be effected by heap, tank or vat leaching techniques. The oxidants are advantageous in that precious metal recovery may be effected in a completely or substantially oxygen-free (or inert gaseous) atmosphere. In this application, the partial pressure of molecular oxygen is preferably no more than about 0.05 atm and more preferably no more than about 0.001 atm while that of the inert gas (such as nitrogen) is preferably at least about 1.0 atm and more preferably at least about 1.1 atm. Certain oxidants such as molecular oxygen can cause rapid degradation of thiosulfate to polythionates, which can complicate precious metal recovery from the pregnant leach solution.

The present invention, in various embodiments, includes components, methods, processes, systems and/or apparatus substantially as depicted and described herein, including various embodiments, subcombinations, and subsets thereof. Those of skill in the art will understand how to make and use the present invention after understanding the present disclosure. The present invention, in various embodiments, includes providing devices and processes in the absence of items not depicted and/or described herein or in various embodiments hereof, including in the absence of such items as may have been used in previous devices or processes, e.g., for improving performance, achieving ease and/or reducing cost of implementation.

The foregoing discussion of the invention has been presented for purposes of illustration and description. The foregoing is not intended to limit the invention to the form or forms disclosed herein. In the foregoing Detailed Description for example, various features of the invention are grouped together in one or more embodiments for the purpose of streamlining the disclosure. This method of disclosure is not to be interpreted as reflecting an intention that the claimed invention requires more features than are expressly recited in each claim. Rather, as the following claims reflect, inventive aspects lie in less than all features of a single foregoing disclosed embodiment. Thus, the following claims are hereby incorporated into this Detailed Description, with each claim standing on its own as a separate preferred embodiment of the invention.

Moreover, though the description of the invention has included description of one or more embodiments and certain variations and modifications, other variations and modifications are within the scope of the invention, e.g., as may be within the skill and knowledge of those in the art, after understanding the present disclosure. It is intended to obtain rights which include alternative embodiments to the extent permitted, including alternate, interchangeable and/or equivalent structures, functions, ranges or steps to those claimed, whether or not such alternate, interchangeable and/or equivalent structures, functions, ranges or steps are disclosed herein, and without intending to publicly dedicate any patentable subject matter.

What is claimed is:

1. A method for recovering a precious metal from a subsurface precious metal-containing material comprising:
   providing a lixiviant, the lixiviant including thiosulfate and an oxidant that is at least one of bromate (BrO\textsuperscript{2−}), chloride (ClO\textsubscript{2}−), chromate (CrO\textsubscript{4}\textsuperscript{2−}), iodate (IO\textsubscript{3}−), ferric oxide (Fe\textsubscript{2}O\textsubscript{3}) and manganese dioxide (MnO\textsubscript{2}); and contacting the lixiviant with the precious metal-containing material while the precious metal-containing material remains subsurface to dissolve the precious metal and form a pregnant leach solution.

2. The method of claim 1, wherein the oxidant includes at least one of chlorite, bromite, iodate, and manganese dioxide.

3. The method of claim 2, wherein the oxidant includes chlorite.

4. The method of claim 2, wherein the oxidant includes bromate.

5. The method of claim 2, wherein the oxidant includes iodate.

6. The method of claim 2, wherein the oxidant includes manganese dioxide.

7. The method of claim 1, wherein the contacting step comprises:
   passing the lixiviant into an injection well; and
   injecting the lixiviant into the precious metal-containing material.

8. The method of claim 7, further comprising:
   collecting the pregnant leach solution in a collection well.

9. The method of claim 1, wherein the precious metal-containing material is unexcavated.

10. The method of claim 1, wherein the lixiviant has a pH of at least about 6.5.

11. The method of claim 9, wherein the lixiviant further comprises at least one of a suspension agent, a thickening agent, and a gelling agent.

12. The method of claim 11, wherein the lixiviant further comprises a suspension agent.

13. The method of claim 11, wherein the lixiviant further comprises a gelling agent.

14. The method of claim 1, wherein the lixiviant comprises no more than about 2 ppm dissolved molecular oxygen.

15. The method of claim 14, wherein the lixiviant comprises at least about 5 ppm cupric ion and at least about 1 ppm ammonia.

16. The method of claim 1, wherein the lixiviant comprises a surfactant.

17. The method of claim 1, wherein at least some of the oxidant is sparingly soluble in the lixiviant.

18. A precious metal product recovered by the method of claim 1.

19. A method for recovering a precious metal from a precious metal-containing material comprising:
   providing a lixiviant, the lixiviant comprising (i) a leaching agent that is at least one of thiosulfate, a halogen in elemental form, and malononitrile and (ii) an oxidant that is at least one of bromate, chlorite, iodate, ferric oxide, chromate, and manganese dioxide; and contacting the lixiviant with a precious metal-containing material to form a pregnant leach solution comprising at least one precious metal dissolved from the precious metal-containing material, wherein, in the contacting step, the dissolved molecular oxygen content of the lixiviant is no more than about 2 ppm.

20. The method of claim 19, wherein the oxidant is insoluble in the lixiviant, wherein the oxidant has a P\textsubscript{50} size of no more than about 100 μm.
21. The method of claim 20, wherein the precious metal-containing material is in a subsurface deposit during the contacting step and the lixiviant comprises a gelling agent.

22. The method of claim 20, wherein the lixiviant comprises a suspension agent.

23. The method of claim 20, wherein the lixiviant comprises a thickening agent.

24. The method of claim 20, wherein the lixiviant comprises a surfactant.

25. The method of claim 19, wherein the precious metal-containing material is unexcavated and is in a subsurface location.

26. The method of claim 19, wherein the contacting step occurs in a stirred tank in the absence or substantial absence of molecular oxygen.

27. The method of claim 19, wherein in the contacting step the material has been excavated and formed into a heap.


29. A method for recovering a precious metal from a subsurface deposit, comprising:

- providing a lixiviant, the lixiviant comprising (i) a leaching agent that is at least one of thiosulfate, a halogen in elemental form, and malononitrile and (ii) an oxidant that is at least one of chlorite (ClO$_2^-$), chlorate (ClO$_3^-$), bromate (BrO$_3^-$), iodate (IO$_3^-$), ferric oxide (Fe$_3$O$_4$), chromate (CrO$_4^{2-}$) and manganese dioxide (MnO$_2$); and

- contacting the lixiviant with the precious metal-containing deposit to form a pregnant leach solution comprising at least one precious metal dissolved from the precious metal-containing material.

30. The method of claim 29, wherein the oxidant is sparingly soluble in the lixiviant and wherein the oxidant has a P$_{90}$ size of no more than about 100 μm.

31. The method of claim 30, wherein the oxidant comprises an oxide of manganese and/or an oxide of a halogen.

32. The method of claim 30, wherein the lixiviant comprises a gelling agent.

33. The method of claim 30, wherein the lixiviant comprises a suspension agent.

34. The method of claim 30, wherein the lixiviant comprises a thickening agent.

35. The method of claim 30, wherein the lixiviant comprises a surfactant.

36. The method of claim 30, wherein the precious metal-containing material is unexcavated and is in a subsurface location.

37. The method of claim 29, wherein the oxidant includes at least one of chlorite, bromate, iodate, and manganese dioxide.

38. The method of claim 37, wherein the oxidant includes chlorite.

39. The method of claim 37, wherein the oxidant includes bromate.

40. The method of claim 37, wherein the oxidant includes iodate.

41. The method of claim 37, wherein the oxidant includes manganese dioxide.

42. The method of claim 29, wherein the contacting step comprises:

- passing the lixiviant into an injection well; and

- injecting the lixiviant into the precious metal-containing material.

43. The method of claim 42, further comprising:

- collecting the pregnant leach solution in a collection well.

44. The method of claim 29, wherein the precious metal-containing material is unexcavated.

45. The method of claim 29, wherein the lixiviant has a pH of at least about 6.0.

46. The method of claim 30, wherein the lixiviant is thiosulfate.

47. The method of claim 46, wherein the lixiviant comprises no more than about 2 ppm dissolved molecular oxygen.

48. The method of claim 46, wherein the lixiviant comprises at least about 5 ppm cupric ion and at least about 1 ppm ammonia.

49. A precious metal product recovered by the method of claim 29.

* * * * *